MORPHOLOGY OF PHASE SEPARATING COPOLYMER MIXTURES(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

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Phase separation of copolymer mixtures reveals various types of domain morphology since both microphase and macrophase separations take place simultaneously. We will describe some recent results of computer simulations of copolymer-homopolymer mixtures in two dimensions emphasizing a new type of pattern and a morphological transition of domains.

1 Introduction

One of the characteristic features of block copolymers is that when the two segments are immiscible the system undergoes a microphase separation at low temperatures. That is, domains of new phases do not grow macroscopically, as in a polymer blend, but cease to grow in a mesoscopic scale due to the chain connectivity. Thus a spatially periodic structure of domains in a mesoscale appears in final equilibrium [1]. Experiments by transmission electron microscopy and scattering techniques have indeed identified various domain structures [2].

Copolymer mixtures provide us with a variety of domain morphology since both macro- and micro-phase separations take place simultaneously. (Equilibrium property has been studied by a mean field theory [3].) One may expect a multiple domain structure in a sense that microphase separated domains are developed in a macrophase separated domain [4], [5].

In this paper, we investigate the kinetics and the domain morphology in the phase separation of copolymer mixtures by computer simulations in two dimensions. The growth behavior is analyzed by calculating the scattering functions. An interfacial approach is applied to confirm the relative stability of the domain patterns.

In the next section, we introduce our model equations. In section 3, the results of simulations are presented. A morphological transition of multiple domain structures is found. Kinetics of domain growth is discussed in section 4.

2 Time-evolution equation

We consider a mixture of AB-type copolymer and C homopolymer having the molecular weights N_i $(i = A, B, C)$ with $N_A = N_B$. It is convenient to choose the independent variables in the combination of the local volume fractions ϕ_A, ϕ_B and ϕ_C as $\psi = \phi_A + \phi_B$ and $\phi = \phi_A - \phi_B$. The variable ψ is the local volume fraction of the AB copolymers and hence it is a measure of the macrophase separation whereas ϕ provides the degree of the microphase separation.

The free energy of this mixture is obtained by generalizing the method in Ref. [6] and is given by

$$F[\phi, \psi] = F_S[\phi, \psi] + F_L[\phi, \psi] \tag{1}$$

The short range part F_S is written in terms of ϕ and $\eta = \psi - \psi_c$ with ψ_c the volume fraction at a macrophase separation temperature as

$$F_S = \int d\vec{r}[\frac{c_1}{2}(\vec{\nabla}\eta)^2 + \frac{c_2}{2}(\vec{\nabla}\phi)^2 + W(\eta, \phi)] \tag{2}$$

where we set $c_1 = c_2 = 0.5$. The local part W is given by

$$W(\eta, \phi) = g_0(\eta) + g_1(\phi) + b_1\eta\phi - \frac{b_2}{2}\eta\phi^2 \tag{3}$$

The potentials g_0 and g_1 take the form given through the relation $dg_i(x)/dx = -A_i \tanh(x) + x$ where we put $A_0 = 1.3$ and $A_1 = 1.1$.

The long range part F_L is written as

$$F_L = \frac{\alpha}{2}\int d\vec{r}d\vec{r}' G(\vec{r} - \vec{r}')\delta\phi(\vec{r})\delta\phi(\vec{r}') \tag{4}$$

where $\alpha \propto (2/N_A)^2$, $-\nabla^2 G(\vec{r} - \vec{r}') = \delta(\vec{r} - \vec{r}')$ and $\delta\phi = \phi - \bar{\phi}$ with $\bar{\phi}$ the spatial average of ϕ. Any bilinear interactions that involve η are not present for $N_A = N_B$.

We have carried out computer simulations of the following time-evolution equations [7]

$$\frac{\partial\eta}{\partial t} = \nabla^2\frac{\delta F_S}{\delta\eta} \tag{5}$$

$$\frac{\partial\phi}{\partial t} = \nabla^2\frac{\delta F_S}{\delta\phi} - \alpha\delta\phi(\vec{r}) \tag{6}$$

A discritized version of Eq. (6) with $\eta = 0$ has been studied for pure block copolymer [8]. In the simulations a two-dimensional space is divided into 128×128 square cells with the periodic boundary conditions. The cell size is set to be unity. The initial conditions are the spatially uniform distributions $\eta = \bar{\eta}$, $\phi_i = \bar{\phi}_i$ at each cell with small random fluctuations superimposed. Note that $\bar{\phi}_i = 0$ when $N_A = N_B$. Starting from these initial conditions we solve Eqs.(5) and (6) numerically with the time increment $\Delta t = 1$.

3 Domain morphology and kinetics

Here we focus our attention on the domain structures obtained by changing the coupling constant b_1. Figures 1 display the domain patterns at $t = 16000$ and $t = 64000$ from top to bottom for $\bar{\eta} = -0.2$, $\bar{\phi} = 0$, $\alpha = 0.02$, $b_2 = 0.2$ and (a) $b_1 = 0.05$ and (b) $b_1 = 0.03$. A copolymer-rich domain for $\eta > 0$ is drawn by gray color whereas a homopolymer-rich domain for $\eta < 0$ is indicated by white color. Regions where ϕ is larger than 0.15 is shown by black color.

It should be noted in Fig. 1a that in the most parts of the copolymer-rich domains, the lamellar stripes tend to be parallel to the interfaces separating copolymer-rich and homopolymer-rich domains so that an onion-ring pattern appears. In Fig. 1b, on the other hand, one can see that the striped domains are formed perpendicularly to the interfaces. Comparing these Figures, one finds that there is a clear morphological transition. We have examined the b_1-dependence in detail and found that the morphological change occurs at about $b_1 = 0.04$.

One notes that the number of circular domains in Fig. 1a is almost time-independent and hence the domain growth is frozen for the parallel configuration. On the other hand, one can see an ordinary domain growth of polymer blends for the perpendicular configuration in Fig. 1b in such a way that larger domains grow further at the expense of smaller domains. This is a clear evidence that domain morphology affects its kinetics.

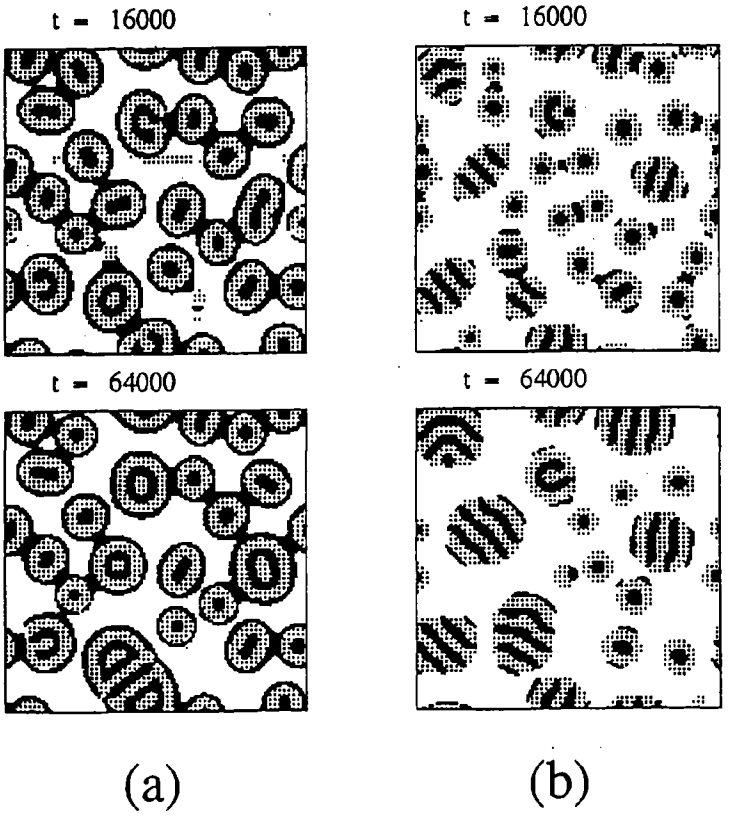

Fig. 1, (a) Parallel and (b) perpendicular morphology

4 Discussions

We have found a morphological transition of growing domains in a mixture of copolymer and homopolymer. When the interaction parameter b_1 is small, lamellar domains tend to align perpendicularly to a macrointerface whereas, when b_1 is large, those take a parallel geometry. This morphological transition can be understood by calculating the interfacial energies. The result indicates that there is a critical value b_1^c of b_1 such that the parallel structure is more stable when $b_1 > b_1^c$. This critical value depends on α as $b_1^c \sim \alpha^{-1/2}$. This implies that the long range interaction is crucial for the parallel morphology. If $\alpha \to 0$, b_1^c becomes infinite. Thus when the long range interaction is absent, the parallel configuration cannot exist.

We have confirmed by computing the scattering functions that kinetics of domain growth in Figs 1a and b is quite different from each other. The growth behavior of the perpendicular configuration is essentially the same as that of spinodal decomposition in polymer blends. On the other hand, the domain growth in the parallel configuration especially for the average volume fraction $\bar{\eta} = -0.2$ is quite slow once a concentric pattern is formed in a copolymer-rich domain.

The present model equations are easily extended to copolymer-copolymer mixtures [9]. For instance, one may examine the phase separation of copolymers having different molecular weights where two kinds of lamellar domains with different periods are formed. In fact, as the phase separation proceeds, one may observe an interconnecting incommensurate lamellar pattern. Its kinetics also differs from that in pure block copolymers and/or homopolymer blends.

The author is grateful to A. Ito and M. Motoyama for their collaboration.

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